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(54) **Title:** PROCESS FOR REGENERATING ION-EXCHANGE RESINS

(57) **Abstract:** The present invention relates to a process for regenerating ion-exchange resin that has been previously used to remove DOC from water in a water treatment plant. The resin is generated by contacting the resin with a chloride salt.

PROCESS FOR REGENERATING ION-EXCHANGE RESINS

FIELD OF THE INVENTION

The present invention relates to water treatment, and in particular to water treatment processes which involve the use of ion-exchange resins. The invention relates to a process for regenerating ion-exchange resin used in such processes, and especially, magnetic ion-exchange resin. For convenience, the invention will be described with reference to the treatment of raw water to produce potable water for distribution and consumption, however it is to be understood that the invention may also be used in other industrial applications, such as in the treatment of sewage and effluent from industrial processes.

BACKGROUND OF THE INVENTION

The processes used in water treatment depend largely on the nature of the raw water. Water supplies which feed industrial plants for the production of potable water for distribution and consumption often contain unacceptably high levels of dissolved, dispersed or suspended organic compounds and materials. Most organic compounds, and materials found in raw water supplies are natural organic matter (NOM). A fraction of the NOM in the raw water supply is represented by dissolved organic compounds which present particular difficulties. These organic compounds referred to as dissolved organic carbon (DOC) are one of the main causes of water discolouration. DOC often includes compounds such as humic and fulvic acids which are water soluble at certain water pH levels. Humic and fulvic acids are not discrete organic compounds but mixtures of organic compounds formed by the degradation of plant residues.

The removal of DOC and especially humic and fulvic acids, from water is necessary in order to provide high quality water suitable for distribution and consumption. A majority of the compounds and materials which constitute DOC are soluble and not readily separable from the water. The DOC present in raw water renders conventional treatment difficult and expensive.

The production of safe potable water from a raw water supply often requires treatment of water to make it aesthetically acceptable, as well as being safe to drink. The removal of suspended matter and DOC is an important aspect of this treatment. Two approaches are commonly used for the removal of suspended matter and DOC. One involves coagulation and the other membrane filtration.

In the process involving coagulation, a coagulant is applied to destabilise and combine with suspended matter and DOC so that they coalesce and form a floc, which can then be physically removed by methods such as floating, settling, filtration or a combination thereof. Coagulants such as alum (aluminium sulphate), various iron salts and synthetic polymers are commonly used in processes for water treatment. However, many raw water sources have high levels of DOC present, which reacts with the coagulant requiring a higher coagulant dose than would be required for removal of suspended matter alone. The bulk of the floc formed may then be removed by sedimentation or flotation and the water containing the remainder of the floc passed through a filter for final clarification. However, even after such treatment, the treated water may contain as much as 30-70% of the initial DOC.

In the membrane filtration process the water is filtered through the membrane. There are four commonly available membrane processes currently used in water treatment. Microfiltration (MF) and Ultrafiltration (UF) are two processes generally used to remove turbidity and solid particles from water. However, where the water contains high levels of DOC these membranes tend to be fouled by the DOC, thereby reducing the flux across the membrane, reducing the life of the membranes and increasing operating costs. The two other membrane processes, Nanofiltration (NF) and Reverse Osmosis (RO) are typically used to remove low molecular weight compounds from water, including dissolved organic carbon (DOC), to allow its use as potable water (e.g. demineralisation). They are also used in desalination of seawater and brackish waters. These membrane systems are designed to handle water containing high levels of DOC and have much higher capital and operating costs than MF and UF for the production of potable water.

Ion-exchange resins can also be used for removing DOC present in raw water. Ion-exchange techniques conventionally involve passing water through a packed bed or column of ion-exchange resin. Target species (DOC) are removed by being adsorbed onto the ion-exchange resin. Ion-exchange resins can be used to remove up to 90% of the DOC in raw water.

Ion-exchange resins may also be used in conjunction with other methods of water purification including those mentioned previously. Sufficient resin may be added to remove a percentage of the DOC such that the cost of any subsequent treatment used to meet water quality objectives is minimised. For example, the use of ion-exchange resin for the removal of DOC can facilitate the reduction of the amount of coagulant required to achieve acceptable product water quality. Ion-exchange resin may also aid in significantly reducing the capital and operating costs of membrane filtration.

In order to further minimise costs in water processing, ion-exchange resins are preferably recyclable and regenerable. Recyclable resins can be used multiple times without regeneration and continue to be effective in adsorbing DOC. Regenerable resins are capable of being treated to remove adsorbed DOC, and as such, these regenerated resins can be reintroduced into the treatment process.

Ion-exchange resins incorporating dispersed magnetic particles (magnetic ion-exchange resins) readily agglomerate due to the magnetic attractive forces between them. This property renders them particularly useful as recyclable resins as the agglomerated particles are more readily removable from the water. A particularly useful magnetic ion-exchange resin for the treatment of raw water is described in WO96/07675, the entire contents of which is incorporated herein by reference. The resin disclosed in this document has magnetic particles dispersed throughout the polymeric beads such that even when they become worn through repeated use, they retain their magnetic character. Ion exchange beads of the type disclosed in this document are available from Orica Australia Pty. Ltd. under the trademark, MIEX®.

WO 96/07615, the entire contents of which is incorporated herein by reference, describes a process for removing DOC from water using an ion-exchange resin which can be recycled and regenerated. This process is particularly useful in treating raw water with magnetic ion-exchange resin of the type described in WO96/07675.

The preferred ion-exchange resins disclosed in WO96/07675 are magnetic ion-exchange resins which have, throughout their structure, cationic functional groups which provide suitable sites for the adsorption of DOC. These cationic functional groups possess negatively charged counter-ions which are capable of exchanging with the negatively charged DOC. Accordingly, the negatively charged DOC is removed from the raw water through exchange with the resin's negative counter ion. As a result of this process DOC becomes bound to the magnetic ion-exchange resin and the function of the ion-exchange resin is reduced. Such resins are referred to herein as used or loaded ion-exchange resins. For producing potable water for distribution and consumption it is particularly important to be able to regenerate the used magnetic ion-exchange resin in an efficient and cost effective manner.

WO 96/07615 discloses a process for regenerating magnetic ion-exchange resin by contacting it with brine (which is substantially a NaCl solution). The by-product of this regeneration process, referred to as the "spent regenerant", is primarily a mixture of the removed DOC and brine. Although not discussed in the specification the spent regenerants of this process are either ultimately disposed of as land fill or discharged into the ocean.

The spent regenerant is usually disposed of by land application when the water treatment is carried out in inland areas where ready access to the ocean is not available. It has been estimated that in the process described in WO96/07615, every million litres of raw water treated per day, generates approximately 200–400 litres of spent regenerant depending on the raw water quality. This method for disposing of spent regenerant can be environmentally unacceptable in many inland areas. In particular, the large concentrations of deposited brine which are produced as a by-product cause degradation of soil quality.

Studies have also attributed the high concentrations of sodium in the spent regenerant to an increase in soil salinity and water logging.

SUMMARY OF THE INVENTION

The present invention provides a process for regenerating ion-exchange resin which has been previously used to remove DOC from water in a water treatment plant, which process comprises contacting the ion-exchange resin with an aqueous solution of a chloride salt for a time and under conditions sufficient to regenerate the resin, wherein said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$,or $CaCl_2$ or mixtures thereof.

In a second aspect the invention provides an industrial scale process for the removal of DOC from water containing DOC, said process comprising:

(i) contacting the water with ion exchange resin to enable adsorption of DOC on the resin;

(ii) separating the resin loaded with DOC from the water; and,

(iii) regenerating at least a portion of the separated resin by contacting the resin with an aqueous solution of a chloride salt for a time and under conditions sufficient to regenerate the resin, wherein said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$, or $CaCl_2$ or mixtures thereof; and

(iv) separating the regenerated resin from the aqueous solution of chloride salt.

In a third aspect the present invention provides an industrial scale process for the removal of DOC from water containing DOC, said process comprising:

(i) contacting the water with ion-exchange resin to enable adsorption of DOC on the resin;

(ii) separating the resin loaded with DOC from the water;

(iii) regenerating at least a portion of the separated resin and recycling the remainder to step (i), wherein the resin is regenerated by contacting the resin with an aqueous solution of a chloride salt for a time and under conditions sufficient to regenerate the resin, wherein the said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$ or mixtures thereof;

(iv) separating the regenerated resin from the aqueous solution of chloride salt; and

(v) recycling the regenerated resin back to step (i).

The process according to the second and third aspects may further include additional steps associated with ion-exchange processes for water treatment, as would be understood by a person skilled in the art.

DESCRIPTION OF PREFERRED EMBODIMENTS

The expression "regenerating ion-exchange resin" as used herein refers to a process in which the ion-exchange capacity of a used ion-exchange resin is returned to a level whereby it is rendered suitable for use in subsequent ion-exchange processes. The ion-exchange resins used in the removal of DOC have cationic groups which provide suitable sites for the adsorption of the DOC. These cationic groups have associated anions which exchange with the DOC during the ion-exchange process. The regeneration process of the present invention involves the displacement (or exchange) of the adsorbed DOC with chloride ions. It is not necessary for all ion-exchange sites in a resin to be regenerated for an ion-exchange resin to be considered "regenerated" for the purpose of the present invention. It is sufficient that the regeneration process has occurred to an extent that ion-exchange resin is useful in subsequent ion-exchange processes. Preferably more than 80% of the ion-exchange sites previously taken up by the DOC or other compounds are

regenerated, more preferably greater than 90% and most preferably greater than 98%.

The ion-exchange resin which is subjected to the regeneration process of the present invention is resin having cationic groups which has been previously used in a water treatment plant to remove DOC from water. The water treatment plant may be a plant for producing potable water for distribution and consumption, or may be a plant for the treatment of sewage, or industrial waste water containing DOC. An industrial water treatment plant may be associated with food processing, pharmaceutical production, electronic component manufacture, membrane plant reject, hospital application and the like. While the present invention is useful in any large scale water treatment facility, it is particularly preferred for use in the treatment of a water source to produce potable water for distribution and consumption.

The used or loaded ion-exchange resin (which is bound by DOC) may be contacted with the aqueous solution of the chloride salt (hereinafter referred to as "the regenerant") in any convenient way which allows the chloride ions to exchange with DOC adsorbed on the resin. Preferably the regenerant is contacted with the ion-exchange resin in a way which allows the recovery of the regenerated ion-exchange resin from the regenerant. In a typical process the regenerant will be added to the used resin and dispersed for a time and under conditions sufficient to allow desorption of the DOC from the resin. The resin may be dispersed in the regenerant by any convenient means, preferably with agitation by mechanical stirring or gas bubble agitation.

Separation of the resin from the regenerant can be achieved by allowing the resin to settle or by filtering through a mesh of appropriate porosity. The regenerant can be recycled and reused to regenerate resin a number of times before it becomes unsuitable for use in the regeneration process.

An alternative process for contacting the used resin with the regenerant involves packing the resin into a column and passing the regenerant through the column. It has been found that such a process generally requires less regenerant than the process described above and

is particularly suitable for the resin described in WO96/07675 due to its structure. This process also enables high rates of desorption of the DOC from the resin and improves the recyclability of the resin.

The preferred resins for the regeneration according to the present invention are magnetic ion-exchange resins, such as the resin disclosed in WO96/07675. These ion-exchange resins which contain magnetic particles agglomerate in a process sometimes referred to as "magnetic flocculation", due to the attractive magnetic forces between them. This property renders them particularly suited to this application as the agglomerated particles are more readily removable from the regenerant. In dispersing the magnetic ion-exchange resin in the regenerant it is important that sufficient shear is applied to overcome the magnetic attractive forces which cause agglomeration. Agglomeration of the resin is achieved by removing the shear causing the resin particles to disperse. The magnetic ion-exchange resin is more dense than the regenerant such that it has a tendency to settle quickly to the bottom of the regeneration tank. This also facilitates the separation of the resin from the regenerant.

The resin may be collected by various means including vacuum collection, filtration, magnetic transport such as belts, pipes, dishes, drums, pumps and the like. Preferably the resin is separated from the regenerant by either vacuum filtration of the regenerant through a filter cloth or mesh of appropriate porosity or by decanting off the regenerant sitting on top of the settled resin or a combination of both. Preferably the separation and collection means do not cause undue mechanical wear which may lead to alteration of the resin. It is also possible to regenerate the magnetic resin by packing it into a column as described above. These regeneration processes are performed in a batch manner. However, continuous processes for regeneration of the ion exchange resin are also possible with the use of belts, drums, pumps, magnetic transport and the like allowing this to occur.

The regenerant of the present invention is preferably a concentrated aqueous chloride salt solution selected from KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$. Preferably the chloride salt is KCl, NH_4Cl, or $MgCl_2$. More preferably the regenerant salt is KCl or NH_4Cl. The most

preferred regenerant salt is KCl.

The concentrated aqueous chloride salt solution used in the process of the present invention are preferably solutions in which the chloride salt concentration is more than 1.5M or more preferably 2M or greater.

The main advantage of the present invention is that the spent regenerants do not contain high levels of sodium and therefore do not contribute to increased salinity when disposed of by land application. As such, the present invention provides an environmentally friendly alternative to the prior art processes. This is of particular benefit for inland water processing plants which do not have ready access to allow for the spent regenerant to be discharged into the ocean.

Furthermore, when using KCl or NH_4Cl as the regenerant the spent regenerant may be utilised as a fertiliser or stock feed. Accordingly, another advantage of using the alternative regenerants of the present invention is that the spent regenerant can be beneficially used in other industries as products such as a fertiliser, a component of a balanced fertiliser or a stock feed. Further processing of the spent regenerant, using processes such as evaporation or membrane treatment may produce a DOC concentrate suitable for other applications such as a soil conditioner or a health supplement. It has also been implied that fulvic acids (a DOC) may find value as a medicament, in particular, as an antioxidant or to increase the functioning of the immune system. Accordingly, the present invention may provide products which are useful in themselves, or which can be further processed to provide pharmaceutically or agriculturally beneficial compounds.

The spent regenerant of the present invention generally consists of an aqueous solution of the regenerant salt and DOC. Depending on the concentration of the regenerant, the nature of the resin and the process in which the resin was used, the spent regenerant will generally have the regenerant salt and DOC in a weight ratio of around 9:1. The DOC contaminated salt by-products (spent regenerant) do not adversely affect their use as fertilisers or stock feeds.

The regenerant may be added, either as a solid or liquid, as a supplement during the manufacture of a stockfeed. The spent regenerant when used as a stockfeed or fertilizer may be used directly, diluted with an acceptable diluent, or concentrated. It may also be washed prior to use, or used as a dry cake or wet cake (which still contains some moisture).

The regeneration process of the present invention is readily incorporated into existing water treatment facilities which utilise ion-exchange resins. For example, it may be used in conjunction with membrane filtration techniques where ion-exchange resins are incorporated to improve the effectiveness of the membranes, increase the flux across membranes and reduce operating costs. For new installations it may be used where existing membrane filtration techniques are replaced with ion-exchange techniques. If membrane filtration techniques are still required, the present invention can be used where ion-exchange processes are incorporated to significantly reduce the size and hence capital and operating cost of a membrane filtration plant. In fact, the reduction in capital and operating costs may enable consideration to be given to the installation of membrane filtration rather than coagulation/ sedimentation plants thereby substantially reducing the size of the plant and enabling the production of potable water without the addition of chemicals other than for disinfection purposes. Examples of water treatment processes involving ion-exchange are disclosed in WO96/07615, and the present regeneration process can be readily incorporated into these processes.

Many processes rely on ion-exchange to produce high quality water on an industrial scale. These include, but are not limited to, softening (i.e. all salts transformed into sodium salts), demineralisation (removing compounds such as $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$, $MgSO_4$ etc.), nitrate, chromate and uranium removal. These waters can then be used in many wide ranging application such as boiler feedwater, potable water or as high quality process water for the pharmaceutical manufacture, electronic component manufacture and the chemical industry. In order for conventional ion-exchange to be used (i.e. passing water through column of resin) it is necessary that the water being treated is relatively free of particulate matter in order to prevent plugging of the ion-exchange bed. Pretreatment using

sedimentation, coagulation and filtration may be necessary.

At the present time there is very little use of ion-exchange in processes for producing potable water for distribution and consumption, due mainly to the inherent problems in treating such large volumes of water with conventional ion-exchange resin. However, the magnetic ion-exchange resin disclosed in WO96/07675 has proved particularly successful in the treatment of such large volumes of water.

In processes involving such an ion-exchange resin the raw water is generally fed into a continuously stirred tank (contactor) which has a nominal residence time usually of between about 5 and 60 minutes. The magnetic ion-exchange resin is added either directly into this tank or into the raw water in the pipeline feeding this tank. It is in this tank that the majority of the ion-exchange process occurs. Prior to treatment with the ion-exchange resin the water will generally have been screened to remove large particles to protect pumps involved in pumping the water to the treatment plant. It is also possible that the water will have been subjected to one or more pretreatment steps, such as coagulation/ flocculation and subsequent clarification.

From the contactor, the resin and water (resin suspension) is generally passed to a separating stage (settler) where the resin is recovered and recycled. Depending on the density of the resin it may be possible to recover it using gravity sedimentation. Magnetic ion-exchange resins have a strong tendency to agglomerate to form large and fast settling particles, when shear is removed (as occurs in the settler). The agglomerated resin particles settle rapidly and are collected on the bottom of the settler where they may be transferred (e.g. by pumping) back to the head of the treatment plant for reuse in the process. At least a portion (and generally a small portion) of the flow which is to be recycled back to the head of the plant is removed and subjected to the regeneration process. To keep the resin concentration at the required level, fresh, regenerated resin is added to the contactor to make up for the resin not being returned. This ensures the performance of the process is maintained. The resin, after it has been regenerated, may be sent to a "fresh" resin tank before it is added back into the process to make up for resin being sent for regeneration.

With processes involving the use of MIEX® resin, pre-treatment is not usually required to remove solids and turbidity from the water, although the raw water may be screened to remove large particulate matter before it is introduced into a water treatment process.

After separation of the ion-exchange resin from the water it is usual to subject the water to further processing before it is suitable for distribution and consumption. The water may be subjected to a coagulation/ flocculation step followed by clarification. This may be done in a gravity settler. The water may also be subjected to one or more of the filtration steps described above, as well as disinfection. The disinfectant may be added at any stage during the water treatment process. Usually however, disinfectants are added during or at the end of the treatment process such that there is residual disinfectant present in the water supplied to the consumer. This is known as secondary disinfection and most commonly involves the use of chlorine, chloramines and chlorine dioxide. However, in order to achieve disinfection of water ozone, potassium permanganate, peroxone, UV radiation and combinations of the above, can also be used as primary disinfectants.

The water treatment process may also be used in conjunction with other unit processes such as ozonation and treatment using granular activated carbon (GAC). These optional features may be incorporated at any suitable stage during the water treatment process, as would be appreciated by a person skilled in the art.

The regeneration processes of the present invention may be utilised in the above described treatment processes or similar water treatment processes, where an ion-exchange process is incorporated prior to or instead of coagulant addition. Typically, coagulants such as alum (aluminium sulphate), iron salts and synthetic polymers are used following the ion-exchange step. The removal of DOC by ion-exchange results in a substantial reduction in the quantity of coagulant required. In addition, the removal of DOC reduces the requirement for subsequent chemical additions and improves the efficiency and/or rate of coagulation, sedimentation and disinfection. This has a beneficial impact on the water quality produced and the size of most facilities required within the water treatment plant

including sludge handling facilities. Since most plants have equipment for regenerating the ion-exchange resin by contacting with brine, the process of the present invention can be conveniently incorporated without significant change in the overall structure or size of the water treatment plant.

The regeneration process of the present invention can be conveniently adapted for use in continuous ion-exchange processes that presently use brine as a regenerant.

The continuous process differs significantly from conventional ion-exchange process. In conventional ion-exchange columns, the water quality produced deteriorates as the ion-exchange capacity is progressively exhausted. The leakage of undesired ions eventually reaches the point where the product water is not potable. In such an instance, the column must be taken-off line and the resin regenerated.

In contrast to this, a continuous process differs in that the overall ion-exchange capacity is continuously maintained. This leads to the production of water with consistent quality as well as the DOC being controlled at predetermined levels. The ability to maintain the quality of water in such processes stems directly from the incorporation of resin recycling and regeneration steps. Such processes usually incorporate a means for removing and recycling the resin to the front end of the process. However, a small amount of the recycled resin is usually removed to be regenerated. The regenerated resin from the regeneration process is subsequently added to the front end of the process. The present invention can be incorporated into such continuous processes.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be further described with reference to the following non-limiting examples and drawings. However it is to be understood that the particularity of the following description of the invention is not to supercede the generality of the preceding description of the invention.

Brief Description of Drawings:

Referring to the drawings;

Figure 1 is a plot of tannic acid released (mass) from the resin as a function of time for NaCl, KCl, NH_4Cl and $MgCl_2$.

Figure 2 is a plot of tannic acid concentration (cumulative) in the regenerant as a function of the number of regenerations for KCl, NaCl and NH_4Cl.

Figure 3 is a plot of tannic acid released (mass) from the resin as a function of the number of regenerations for NaCl, KCl and NH_4Cl.

Figure 4 is a plot of absorbance at 254nm of the regenerant as a function of the number of regenerations for NaCl, KCl and NH_4Cl.

Figure 5 is a plot of pH of regenerant contacted with resin as a function of the number of regenerations by NaCl, KCl and NH_4Cl.

Figure 6 is a plot of TOC (Total Organic Carbon) of regenerant contacted with resin as a function of the number of regenerations by NaCl, KCl and NH_4Cl.

Figure 7 is a plot of TOC of regenerant contacted with resin as a function of the absorbance at 254nm for NaCl, KCl and NH_4Cl.

Figure 8 is a plot of the chloride concentration of the regenerant contacted with resin as a function of the number of regenerations for the regenerants NaCl, KCl and NH_4Cl.

Examples:

Example 1: Kinetics of Single Regeneration of MIEX® DOC Resin Loaded with Tannic Acid using Various Regenerants.

500ml of MIEX® DOC (Orica Australia Pty. Ltd.) resin was sampled, and washed with

approximately 43 quantities of 1L of deionised water to ensure that there were no resin fines.

210ml of the above resin was placed in a sintered glass column, and was loaded with a solution of 100g of tannic acid (a surrogate material for DOC) in 2L of deionised water. The tannic acid solution was passed through the column over a period of 2 hours. After 30 minutes, the effluent changed in colour from clear to brown. The resin was assumed to be fully loaded with tannic acid after 2 hours.

A 50ml sample (30 mins settling) of the tannic acid loaded resin was taken and washed thoroughly with deionised water before it was added to a 150ml stirred solution (i.e.: 3 bed volumes) of NaCl, which had a chloride concentration of 2.05M. Samples were taken at various time intervals by filtering the suspension through a 3 micron filter cartridge. A sample of the regenerant before resin addition was also taken. The pH was monitored at various times during the contact.

The samples were diluted by a factor of 250, and the concentration of tannic acid in solution was determined by using a Varian Cary 50 Probe UV-VIS spectrophotometer at 275 nm. A standard curve was generated, using standards of 0, 5, 10, 20 and 30 mg/L tannic acid.

The above regeneration was repeated using the regenerants KCl, NH_4Cl and $MgCl_2$. The results are shown in Figure 1.

Example 2: Efficiency of Alternative Regenerants after Multiple Regenerations of MIEX® DOC Resin Loaded with Tannic Acid.

Multiple regenerations of MIEX® DOC resin were simulated using NaCl, KCl, and NH_4Cl.

2000ml of MIEX® DOC resin which had been belt washed over a 40 micron screen, was

obtained. The resin was then washed with 12L of water to remove any residual fines.

The resin sample was stirred in 10L of 20g/L tannic acid solution (ie.:100mg/mL resin) at 450rpm for 1 hour. Samples of the tannic acid solution were taken prior to and after contact with MIEX® DOC resin for UV analysis. The resin was washed with 12L of deionised water and set aside for regeneration. The samples were diluted by 500 times, buffered to pH 7 and the absorbance of each sample at 275nm measured with the UV-VIS spectrophotomer. The amount of tannic acid loaded onto the resin was therefore calculated.

The following was done for each regenerant. 500ml of regenerant solution was made containing 2M chloride content. A sample of regenerant solution was taken for UV analysis. Nine 50ml samples of loaded resin were prepared. The first 50ml resin sample was filtered to remove excess water and was then added to the 150 ml of the above regenerant solution and stirred at 300rpm in a 200ml beaker for 30 minutes. The regenerant was then filtered from the resin, and a 5g sample taken for UV analysis. The chloride concentration of the remaining regenerant was adjusted before the following regeneration by adding and dissolving 4g NaCl, 5g KCl or 3.6g NH_4Cl. This ensured that the chloride concentration was kept at above 2M. The volume was then readjusted to 150ml with deionised water. The volume and mass of extra water required was noted. The regenerant was then contacted with the second 50ml resin sample, as outlined above. A total of nine regenerations were performed for each regenerant. The pH was measured prior to the first, and after the ninth regeneration using pH paper.

The regenerant samples were diluted by 250 times, and pH 7 buffer was added during the dilution to ensure the pH was kept at 7 during UV measurement. The absorbance of each sample was measured. Standards containing 1, 5, 10, 20 and 40mg/l tannic acid, buffered to pH 7 were made. Each sample's absorbance was then converted to mass tannic acid released per volume resin, correcting for the dilutions made after each regeneration. The concentration of tannic acid in the regenerant is plotted as a function of the number of regenerations in Figure 2, while the amount of tannic acid released in a cycle is plotted as a function of the number of regenerations in Figure 3.

Example 3: Efficiency of Alternative Regenerants after Multiple Regenerations of MIEX® DOC Resin Loaded with DOC from Real Water.

A 2.2L sample of MIEX® DOC resin was obtained which had been loaded with NOM from natural waters in a water treatment plant at Wanneroo (Western Australia) The resin was then washed with two quantities of 1L deionised water to remove any iron oxide fines.

The following was done for each regenerant: NaCl, KCl and NH_4Cl:

1) 500 ml of regenerant solution was made containing 2M chloride. A 5g sample of regenerant solution was taken for UV analysis, Total Organic Carbon (TOC) analysis and pH measurement.

2) Ten 50ml samples (measured after 30 mins settling) of the washed resin were prepared.

3) The first 50ml resin sample was filtered for 20mins in a Buchner funnel to remove excess water.

4) This resin was then added to 150ml of the 2M regenerant solution in a 200ml beaker and was stirred at 300rpm using a 3-4 cm flat bladed paddle for 30 minutes.

5) The regenerant was then filtered from the resin, and a 5g sample taken for UV, TOC and pH analysis. The mass and volume of the remaining solution were recorded.

6) The pH of the regenerant sample was determined using a pH electrode. The chloride concentration of the regenerant sample was also determined. The remainder of the sample was kept at 4°C for several days before TOC analysis.

7) The appropriate amount of regenerant salt was added to ensure that the chloride concentration of the final diluted regenerant would be 2M.

8) The volume was then readjusted to 150ml with deionised water. The final volume and mass of the regenerant were noted.

9) The regenerant was then contacted with the next 50ml resin sample, as outlined in steps 3 to 8 above. A total of ten regenerations were performed.

Chloride Measurement

1) 2ml of regenerant was added to a 100ml volumetric flask, and diluted to the mark with deionised water. (Note: 1ml regenerant in 100ml flask used for KCl and NH_4Cl regenerants).

2) 20g of the diluted solution was taken, 3 drops of concentrated HNO_3 were added and the solution was titrated against 0.05M $AgNO_3$ solution using a Metrohm autoburette which automatically calculates chloride content.

UV Measurement

1) The regenerant samples were diluted 1000 times and buffered to pH 7. (i.e., 1.0 ml of sample was placed in a 50ml volumetric flask, and diluted to the mark with deionised water. 2.5ml of this diluted solution was placed in a 50ml volumetric flask, 5ml of pH 7 buffer was added, and the flask was filled to the mark with deionised water.)

2) The absorbance was measured at 254nm using the UV spectrophotometer.

TOC Measurement

1) The regeneration samples were stored at 4°C for several days before TOC measurement (i.e.: 14, 12, and 5 days for NaCl, KCl and NH_4Cl samples respectively).

2) The samples were then diluted 10,000 times and approximately 20ml of the diluted solution was taken for TOC analysis.

The results are shown in Figures 4 to 8.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within the spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for regenerating ion-exchange resin which has been previously used to remove DOC from water in a water treatment plant, which process comprises contacting the ion-exchange resin with an aqueous solution of a chloride salt for a time and under conditions sufficient to regenerate the resin, wherein said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$ or mixtures thereof.

2. A process according to claim 1 wherein the chloride salt is selected from KCl or NH_4Cl, or mixtures thereof.

3. A process according to claim 1 wherein the chloride salt is KCl.

4. A process according to claim 1 wherein the ion-exchange resin is a magnetic ion exchange resin.

5. A process according to claim 1 wherein the ion-exchange resin is contacted with the aqueous solution of a chloride salt by first packing the resin into a column and passing the aqueous solution through the column.

6. A process according to claim 1 wherein the ion-exchange resin is contacted with the aqueous solution of a chloride salt by dispersing the resin in an aqueous solution of the chloride salt and agitating by mechanical stirring.

7. An industrial scale process for the removal of DOC from water containing DOC, said process comprising:

(i) contacting the water with ion exchange resin to enable adsorption of DOC on the resin;

(ii) separating the resin loaded with DOC from the water;

(iii) regenerating at least a portion of the separated resin by contacting the resin with an aqueous solution of a chloride salt for a time and under conditions

sufficient to regenerate the resin, wherein the said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$ or mixtures thereof; and

(iv) separating the regenerated resin from the aqueous solution of chloride salt.

8. An industrial scale process for the removal of DOC from water containing DOC, said process comprising:

(i) contacting the water with ion-exchange resin to enable adsorption of DOC on the resin;

(ii) separating the resin loaded with DOC from the water;

(iii) regenerating at least a portion of the separated resin and recycling the remainder to step (i), wherein the resin is regenerated by contacting the resin with an aqueous solution of a chloride salt for a time and under conditions sufficient to regenerate the resin, wherein the said chloride salt is selected from KCl, NH_4Cl, $MgCl_2$ or $CaCl_2$ or mixtures thereof;

(iv) separating the regenerated resin from the aqueous solution of chloride salt; and

(v) recycling the regenerated resin back to step (i).

9. A process according to claim 7 or claim 8 wherein the chloride salt is selected from KCl or NH_4Cl or mixtures thereof.

10. A process according to claim 7 or claim 8 wherein the chloride salt is KCl.

11. A process according to claim 7 or claim 8 wherein the ion-exchange resin is a magnetic ion exchange resin.

Figure 1

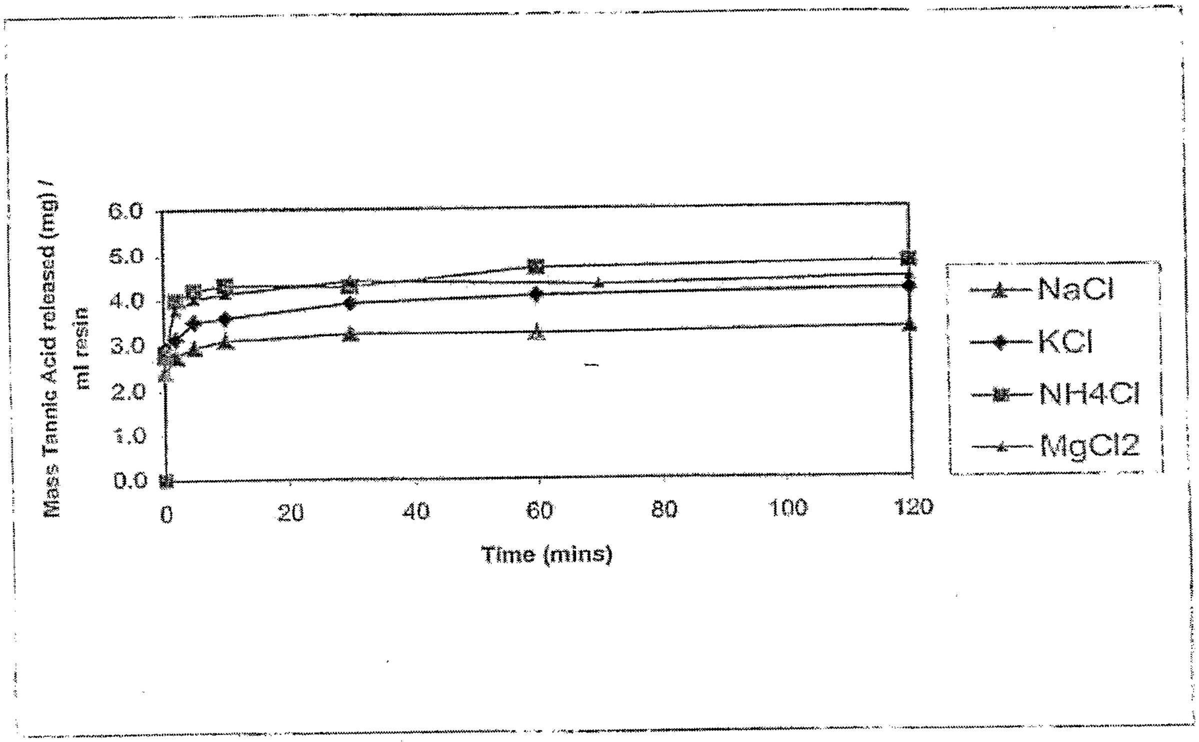

Mass Tannic Acid released (mg) / ml resin
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
100
120
Time (mins)
NaCl
KCl
NH4Cl
MgCl2

Figure 2

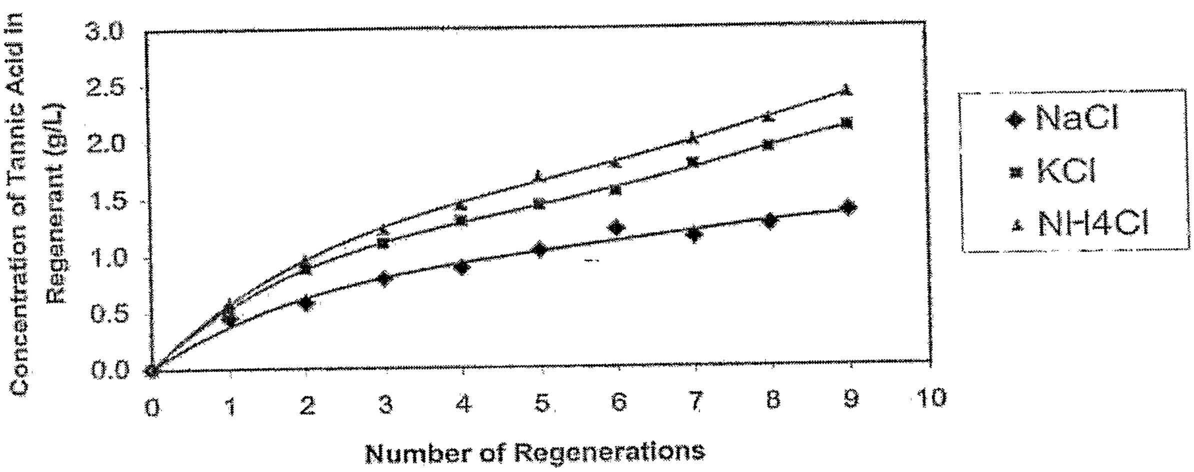

Concentration of Tannic Acid in Regenerant (g/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8
9
10
Number of Regenerations
NaCl
KCl
NH4Cl

Figure 3

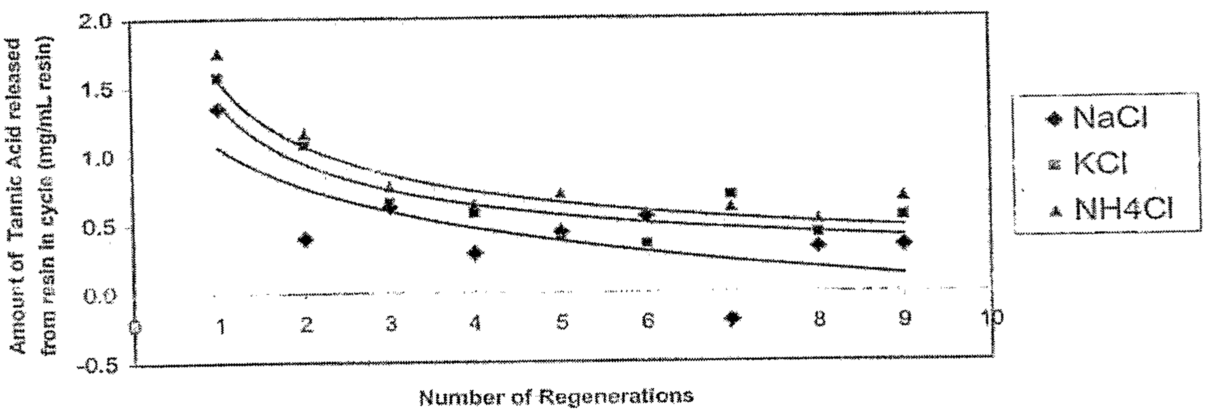

2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
8
9
10
Amount of Tannic Acid released from resin in cycle (mg/mL resin)
Number of Regenerations
NaCl
KCl
NH4Cl

Figure 4

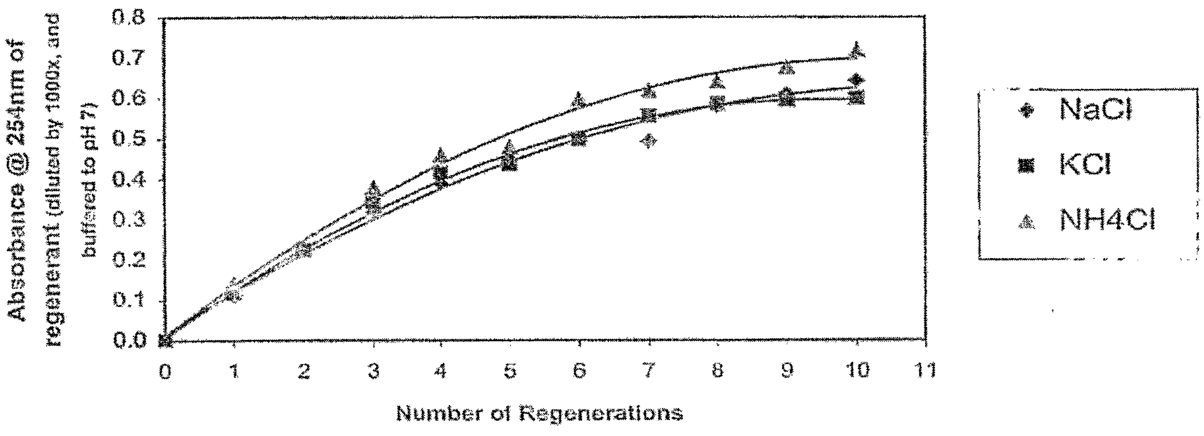

Absorbance @ 254nm of regenerant (diluted by 1000x, and buffered to pH 7)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
Number of Regenerations
NaCl
KCl
NH4Cl

Figure 5

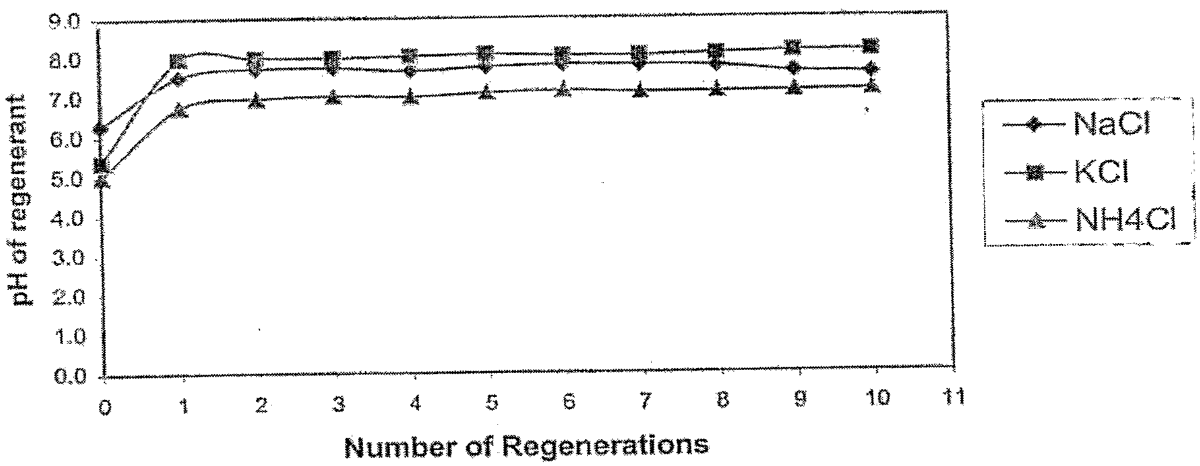

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
pH of regenerant
0
1
2
3
4
5
6
7
8
9
10
11
Number of Regenerations
NaCl
KCl
NH4Cl

Figure 6

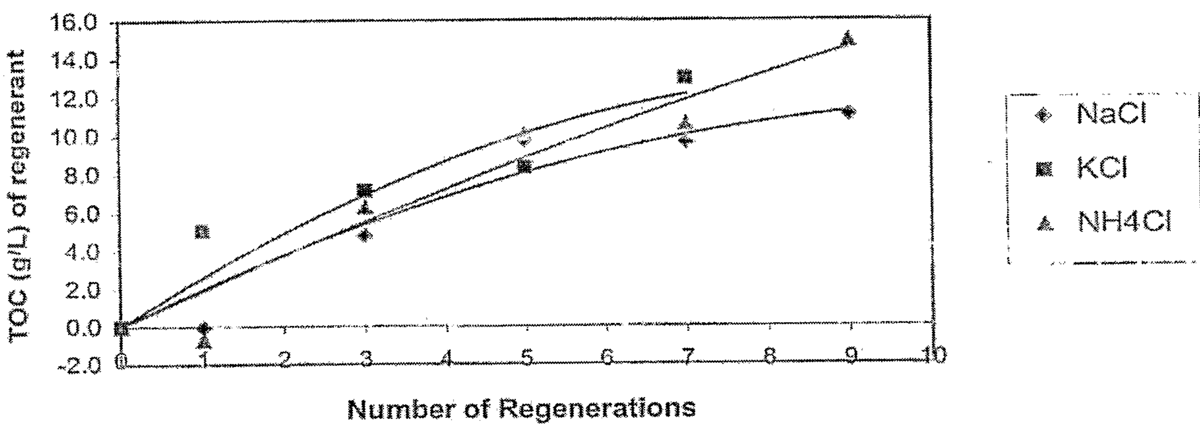

16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
TOC (g/L) of regenerant
0
1
2
3
4
5
6
7
8
9
10
Number of Regenerations
NaCl
KCl
NH4Cl

Figure 7

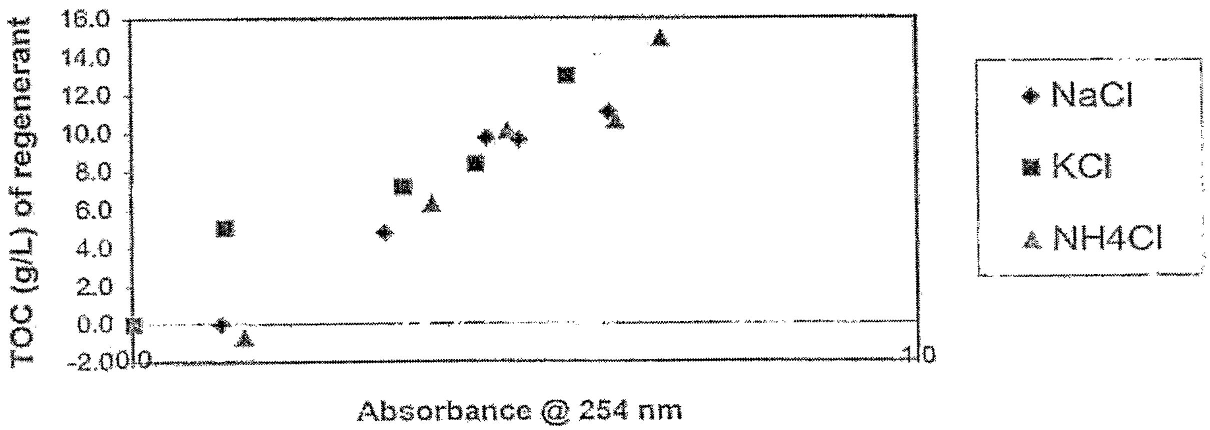
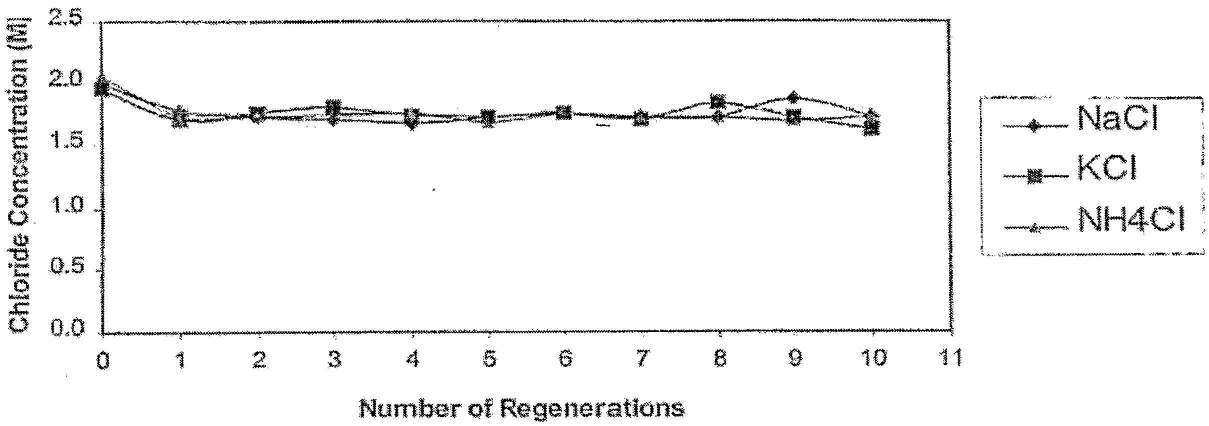

16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.00.0
1.0
TOC (g/L) of regenerant
Absorbance @ 254 nm
NaCl
KCl
NH4Cl

Figure 8


Chloride Concentration (M)
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8
9
10
11
Number of Regenerations
NaCl
KCl
NH4Cl

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00405

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C02F 1/42, B01J 49/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI IPC C02F 1/42, BOIJ 49/00 and Keywords (chloride, KCl, NH_4Cl, $MgCl_2$, $CaCl_2$, ion exchange)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 200124928 A (KONINKLIJKE PHILIPS ELECTRONICS N.V.) 12 April 2001 whole document	1-11
X	Derwent Abstract Accession No. 22537C/13, Class A91, D15, J01 JP 55-020634 A (ASAHI CHEM IND CO LTD) 14 February 1980	1-11
X	Derwent Abstract Accession No. 59193C/34, Class D15, E36 JP 55-088891 A (ASAHI CHEM IND CO LTD) 4 July 1980	1-11

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 April 2003	30 APR 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **ADRIAN GILLMORE** Telephone No : (02) 6283 2125

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2046620 A (ZEST INVESTMENTS LTD.) 19 November 1980 whole document	1-11
X	GB 2085749 A (COAL INDUSTRY (PATENTS) LTD.) 6 May 1982 whole document	1-11
X	EP 838433 A (WEISSENBACHER et al) 29 April 1998 whole document	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU03/00405

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member	
WO	200124928	EP	1137488
JP	55020634	NONE	
JP	55088891	NONE	
GB	2046620	NONE	
GB	2085749	NONE	
EP	838433	NONE	

END OF ANNEX